

## NONFOGGING AND STAINPROOF GLASS ARTICLES

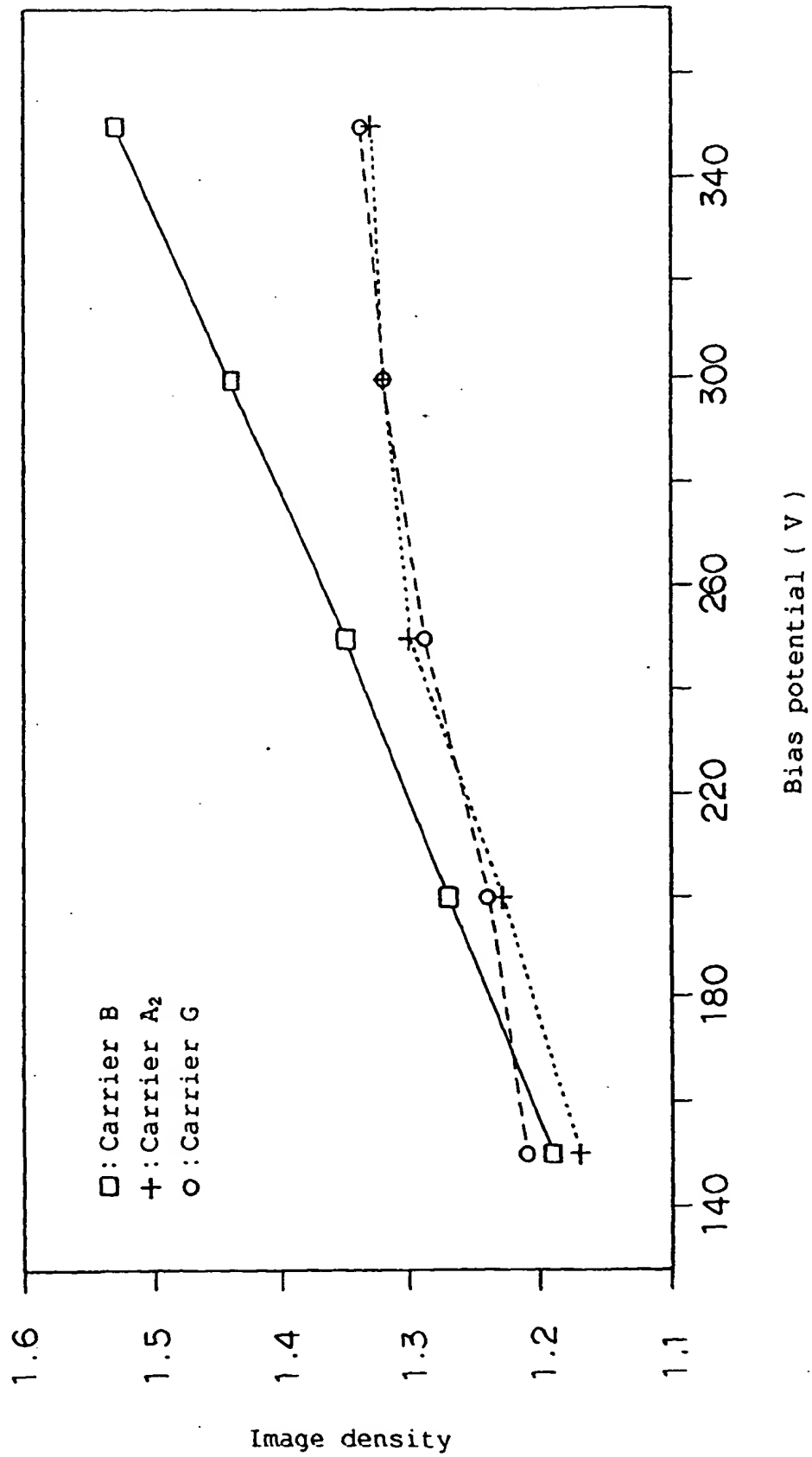
Patent Number: EP0882686  
 Publication date: 1998-12-09  
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 Requested Patent: ☐ EP0882686, A1  
 Application Number: EP19970949132 19971218  
 Priority Number(s): WO1997JP04672 19971218; JP19960337969 19961218; JP19970340904 19971211  
 IPC Classification: C03C17/34  
 EC Classification: C03C17/42, C03C17/34D2  
 Equivalents: ☐ JP10231146, ☐ WO9827021

### Abstract

A carrier for electrophotography making the most of excellent characteristics of a carrier having a polyolefinic resin coating, being freely adjustable of its charge quantity and its static resistance, being also obtainable of an image having a stable density and being able to effectively prevent external additives from being spent due to adhesion of the external additives, and a developer for electrophotography using this carrier. In a carrier for electrophotography including a carrier core material having magnetism and a coating layer consisting of a high molecular weight polyethylene resin covering the surface of the carrier core material, the coating layer consisting of the high molecular weight polyethylene resin includes, at least as the outermost layer, a layer containing magnetic powder the cubic shape of which is a convexed polyhedral body encompassed by at least six flat and/or curved surfaces, or a layer containing this magnetic powder, silica and/or a fine particle resin.

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Fig. 1



## Description

### Technical Field

The present invention relates to a carrier for electrophotography and a developer for electrophotography using the carrier. More particularly it relates to a carrier for electrophotography used in development of an electrostatic latent image in image formation using electrophotography, and to a developer using the carrier.

### Background of the Invention

As an electrostatic latent image development for electrophotography, one-component magnetic jumping development, one-component non-magnetic contacting development, and two-component development, in which development is performed by frictionally electrifying a toner, transporting a developer, and contacting with an electrostatic latent image, by mixing an insulating non-magnetic toner and magnetic carrier particles, are known so far.

Particularly attention has been paid gain to application of the two-component development to the color printer as a promising method in near future.

A particulate carrier, which is used in such two-component development, is usually produced by coating a magnetic carrier core material with an appropriate material in order to prevent filming a toner onto the surface of the carrier, to form a carrier-uniform surface, to elongate the lifetime of a developer, to prevent damage of a sensitizer by a carrier, to control charge quantity, or for other purposes.

Conventional resin-coated carriers are not, however, satisfactory in durability because the coat is easily exfoliated by an impact such as stirring applied when used or for other reasons.

To solve this problem, the inventors developed and proposed a method to form a polyolefin-based resin coat by directly carrying out polymerization of an olefin-based monomer on carrier-core-material particles of materials such as ferrite, as described, for example, in Japanese Patent Laid-open Pub. No. Hei. 2-187771. The polyolefin-based resin-coated carrier obtained according to this method, 1) has the strong adhesion strength between the core material and the coat, 2) does not give any deterioration in the quality of image, 3) is excellent in durability, and 4) is excellent in spent stability, even if copying is repeated continuously for a long time, because the coat is directly formed on the carrier core material particles.

On the other hand, however, this polyolefin-based resin-coated carrier did not have adequate durability, not only because control of charge polarity and adjustment of charge quantity can not be freely conducted, but also because of the problem that the external additives are spent by attachment of external additives of a toner or for other reasons.

In addition, the carrier did not have enough properties which allow fine adjustment of resistance and adjustment of image density.

As methods to solve the above-mentioned problems, a method to improve charge quantity by containing nigrosin in a carrier-coated resin is disclosed in Japanese Patent Laid-open Pub. No. Sho. 53-100242, a method to improve fluidity by adding a fluidity-improving agent is disclosed in Japanese Patent Laid-open Pub. No. Sho. 61-9661, and a method, to prevent making the charging property uniform and being spent by adding one selected from a group consisting of electroconductive fine particles, inorganic filler particles, and a charge-controlling agent, is disclosed in Japanese Patent Laid-open Pub. No. Hei. 2-210365.

These methods, however, could not satisfy both 1) freely controlling charge polarity, adjusting charge quantity, and adjusting resistance, with taking advantage of an excellent property that the above-mentioned polyolefin-based resin-coated carrier has, and 2) preventing external additives of a toner from being spent.

The present invention aims to solve the above-mentioned problems, i.e. the purpose of the present invention is to provide a carrier for electrophotography and a developer using the carrier, which allows adjusting the charge quantity and static resistance freely, with taking advantage of an excellent property that a carrier having a polyolefin-based resin coat has, obtaining an image stable in light and shade, and effectively preventing external additives from being spent by attachment of external additives of a toner.

## Disclosure of the invention

In order to achieve the above object, the present invention provides a carrier for electrophotography having a carrier core material with magnetism and a coating layer made of a high-molecular-weight polyethylene resin for coating the surface of the carrier core material; wherein the coating layer made of the high-molecular-weight polyethylene resin has, at least as its outermost layer, a layer containing a magnetic powder that is a convex polyhedron encompassed by both or either at least six flat and curved planes in the three-dimensional geometry.

As its preferred mode, there is provided the carrier for electrophotography, wherein the coating layer made of the high-molecular-weight polyethylene resin has the above-mentioned magnetic powder and silica.

As its preferred mode, there is provided the carrier for electrophotography, wherein the coating layer made of the high-molecular-weight polyethylene resin has the above-mentioned magnetic powder, silica and a fine particle resin.

As its preferred mode, there is provided the carrier for electrophotography, wherein the average particle diameter of the magnetic powder is in a range of 0.1 to 1  $\mu\text{m}$ .

As its preferred mode, there is provided the carrier for electrophotography, wherein its resistance is in a range of  $1 \times 10^2$  to  $1 \times 10^{14}$   $\Omega \cdot \text{cm}$ .

As its preferred mode, there is provided the developer for electrophotography consisting of the carrier for electrophotography, and a toner that was mixed with the carrier at a weight ratio of 2 to 40wt.% per total amount of the toner and the carrier.

## Brief Description of the Drawing

Fig. 1 is a diagram illustrating the dependence of image density on magnet roller bias potential in Applied Example 1 of the present invention.

Fig. 2 is a diagram illustrating the result of evaluation of continuous printing in Applied Example 2 of the present invention.

## Best Mode for Carrying Out the Invention

The embodiment of a carrier for electrophotography and a developer for electrophotography using the carrier according to the present invention will be explained concretely below.

### I. Carrier for electrophotography

The carrier for electrophotography according to the present invention has a carrier core material and a coating layer consisting of a high-molecular-weight polyethylene resin coating the surface of the carrier core material, wherein said coating layer consisting of a high-molecular-weight polyethylene resin contains a layer containing magnetic powder that is a convex polyhedron that is encompassed by both or either at least six flat and curved planes in the three-dimensional geometry at least as its outermost layer, or a layer containing the above magnetic powder and silica, or a layer containing the above magnetic powder, silica and a fine particle resin.

Each component will be explained concretely below.

#### 1. Carrier core material

##### (1) Material

There is no particular limitation to the core material of carrier according to the present invention. Well

known materials for the two component-system carrier for electrophotography can be used, such as 1) ferrite, magnetite, or the like; metals such as iron, nickel, and cobalt, 2) an alloy or a mixture of these metals with a metal such as copper, zinc, antimony, aluminum, lead, tin, bismuth, beryllium, manganese, magnesium, selenium, tungsten, zirconium, and vanadium, 3) a mixture of the above-mentioned ferrite or the like with a metal oxide such as iron oxide, titanium oxide, and magnesium; a nitride such as chromium nitride and vanadium nitride; a carbide such as silicon carbide and tungsten carbide, and 4) ferromagnetic ferrite, and 5) a mixture of these.

## (2) Geometry and particle size

There is no particular limitation to the geometry. Both or either spherical and irregular forms are acceptable. Although there is no particular limitation to the particle size, a size of 20-100  $\mu\text{m}$  are preferable. If the size is smaller than 20  $\mu\text{m}$ , attachment (scattering) of the carrier to the electrostatic latent image carrier (a sensitizer in general) may occur. If the size is larger than 100  $\mu\text{m}$ , troubles such as carrier streaks may occur and cause deterioration of the quality of image.

## (3) Ratio of formulation

The weight ratio of the carrier core material per the overall carrier is set to 90wt.% or higher, preferably to 95 wt.% or higher. The ratio of formulation indirectly specifies the thickness of the resin-coated layer of the carrier. If the weight ratio is lower than 90wt.%, the coating layer may become too thick, and the durability and the stability of charge which are required for a developer might not be satisfied because of exfoliation of the coating layer, increase in the charge quantity, and other reasons, even if the carrier is practically applied to a developer. Also it may cause troubles such as low reproducibility in fine lines and decrease in image density with respect to the quality of image. Although there is no particular limitation to the upper limit, such a ratio may be enough that the coated resin layer can completely coat the surface of the carrier core material. This value depends on the physical properties of the carrier core material and the method for coating.

## (4) Electroconductive layer

An electroconductive layer can be formed on the carrier core material particles prior to coating with a high-molecular-weight polyethylene resin if necessary.

As the electroconductive layer formed on the carrier core material particles, for example, one, in which electroconductive fine particles are dispersed in an appropriate binding resin, is favorable. The formation of such an electroconductive layer is effective in enhancing a developing property and obtaining clear images having high image density and clear contrast. The reason for this is considered that the existence of the electroconductive layer lowers electroresistance of the carrier to a suitable level to balance leak and accumulation of electric charge.

As the electroconductive fine particle added to the electroconductive layer, the followings can be used: carbon black such as carbon black and acetylene black, carbide such as SiC, magnetic powder such as magnetite, SnO<sub>2</sub>, and titanium black. As the binding resin of the electroconductive layer, the followings can be used: various thermoplastic resins and thermosetting resins such as polystyrene-based resins, poly(meth)acrylic acid-based resins, polyolefin-based resins, polyamide-based resins, polycarbonate-based resins, polyether-based resins, polysulfonic acid-based resins, polyester-based resins, epoxy-based resins, polybutyral-based resins, urea-based resins, urethane/urea-based resins, silicone-based resins, and Teflon-based resins, and a mixture, a copolymer, a block polymer, a graft polymer, and a polymer blend of these resins.

The electroconductive layer can be formed by coating a liquid in which the above-mentioned electroconductive fine particles are dispersed in the above-mentioned appropriate binding resin onto the surface of the carrier core material particles by a method such as the spray coating method and the dipping method. In addition, it can also be formed by melting/blending/crushing the core material particles, electroconductive fine particles, and a binding resin. In addition, it can also be formed by polymerizing a polymerizable monomer on the surface of the core material particle in the presence of the electroconductive fine particles. Although there is no particular limitation to factors such as the size and the amount of addition of the above-mentioned electroconductive fine particles as long as the properties such as electroresistance of the carrier according to the present invention are satisfied, an average particle size of the electroconductive fine particle should be one that allows homogeneous dispersion in the above-mentioned resin solution: concretely 0.01-2  $\mu\text{m}$ , preferably 0.01-1  $\mu\text{m}$ . Although the amount of

the electroconductive fine particles to add also depends on the kind and other factors and it is not possible to specify it, a weight ratio of 0.1-60wt.% per the binding resin of the electroconductive layer, preferably 0.1-40wt.% would be acceptable. Although such a trouble occurs that the reproducibility decreases when fine lines are copied repeatedly using a carrier like this when the packing ratio of the carrier is as small as ca. 90wt.% and the thickness of the coating layer is relatively thick, this kind of trouble can be dissolved by adding the above-mentioned electroconductive fine particles.

The carrier core material particles on which a functional layer such as an electroconductive layer was formed will also be designated hereafter simply as "carrier core material particles" as long as misunderstanding can be avoided.

## 2. Coating layer consisting of high-molecular-weight polyethylene resin

### (1) Molecular weight of resin

High-molecular-weight polyethylene resins, which are usually designated as "polyethylene", having a number-average molecular weight of 10,000 or higher or a weight-average molecular weight of 50,000 or higher are preferably used in the present invention. The followings having a number-average molecular weight lower than 10,000 are generally excluded from the high-molecular-weight polyethylene resins for the present invention: polyethylene wax (Mitsui High Wax, manufactured by Mitsui Petrochemical Industries, Ltd.), Dialene 30 (manufactured by Mitsubishi Gas Chemical Co., Ltd.), Nisseki Lexpole (manufactured by Nippon Oil Co., Ltd.), San Wax (manufactured by Sanyo Chemical Co., Ltd.), Polyrez (neutral wax, manufactured by Polymer Co., Ltd.), Neowax (manufactured by Yasuhara Chemical Co., Ltd.), AC Polyethylene (manufactured by Allied Chemical Inc.), Eporene (manufactured by Eastman Kodak Co.), Hoechst Wax (manufactured by Hoechst Co., Ltd.), A-Wax (manufactured by BASF Co., Ltd.), Polywax (manufactured by Petrolite Co., Ltd.), Escomer (manufactured by Exxon Chemical Co., Ltd.), or the like. The polyethylene wax may be coated by the conventional dipping method and the spray method by dissolving in hot toluene or the like. However, since the mechanical strength of the polyethylene wax is weak, it is exfoliated by the shear in a developing machine after a long-term use or for other reasons.

It is also acceptable to add at least one kind of functional particles such as the above-mentioned electroconductive fine particles and particles having an ability to control the electric charge, which will be described later, into the coating layer consisting of the above-mentioned high-molecular-weight polyethylene resin.

### (2) Method for forming coating layer

There is no particular limitation to form a coating layer used in the present invention. Although well known methods such as the dipping method, the fluidized bed method, the dry-type method, and the spray dry method can be applied, the following polymerization method is preferred to coat the polyethylene-based resin because the resin-coating strength is strong and the coat is not be exfoliated easily.

#### a. Polymerization method

"The polymerization method" is a method to produce a polyethylene resin-coated carrier by treating the surface of the carrier core material with an ethylene-polymerizing catalyst and directly polymerizing ethylene (forming polyethylene) on the surface, as described, for example, in Japanese Patent Laid-open Pub. No. Sho. 60-106808 and Japanese Patent Laid-open Pub. No. Hei. 2-187770. The polyethylene resin-coated layer can be formed by suspending a product that is obtained in advance by contacting a highly active catalytic component that contains both or either titanium and zirconium, and is soluble in a hydrocarbon solvent, such as hexane and heptane, with the carrier core material, and an organoaluminum compound in the above-mentioned hydrocarbon solvent, supplying an ethylene monomer, and polymerizing it on the surface of the carrier core material. In addition, in case fine particles or electroconductive fine particles having the above-mentioned an electric charge-conferring function are added, they can be added while the above-mentioned high-molecular-weight polyethylene resin-coated layer is formed.

As this production forms a polyethylene-coated layer directly on the surface of the carrier core material, a coat excellent in strength and durability is obtained.

If functional fine particles such as electroconductive fine particles and fine particles having an ability to



control electric charge are dispersed/coexisted in the polymerization system in this way, while a high-molecular-weight polyethylene resin coat is growing/being formed by polymerization, the functional fine particles are incorporated into this coat, and a high-molecular-weight polyethylene resin coat containing the functional particles is formed.

#### b. Amount of coating

A high-molecular-weight polyethylene resin coat is formed with a weight ratio of [carrier core material]/[high-molecular-weight polyethylene resin coat] being preferably in a range of 99.5/0.5-90/10, more preferably in a range of 99/1-95/5.

#### c. Addition and supporting of functional fine particles

The quality of the carrier can be improved, as described above, by adding/carrying at least one kind of functional particles, such as electroconductive fine particles and particles having an ability to control electric charge, in the high-molecular-weight polyethylene resin coat.

As electroconductive fine particles which are added/carried in high-molecular-weight polyethylene resin coat, can be used all well-known ones, for example, carbide such as carbon black and SiC, electroconductive magnetic powder such as magnetite, SnO<sub>2</sub>, titanium black. A preferable average particle size of the electroconductive fine particles is 0.01-5.0  $\mu\text{m}$ .

#### (3) Outermost layer

The coating layer has a layer containing magnetic powder that is a convex polyhedron that is encompassed by at least six flat and/or curved planes in the three-dimensional geometry at least as its outermost layer, or a layer containing said magnetic powder and silica and/or fine particle resin.

#### a. Magnetic powder

Magnetite, ferrite, iron powder, or the like can be used as a material for the magnetic powder used in the present invention.

The three-dimensional geometry of the magnetic powder is a convex polyhedron that is encompassed by both or either at least six flat and curved planes. Although "polyhedron" usually means a steric body that is encompassed only with flat planes, "polyhedron" in the present invention is referred to as a solid body that is encompassed with both or either flat and curved planes. The existence of angles and vertices formed by flat and curved planes like this is important.

If the carrier is a polyhedron like this, as the electroconduction changes from the surface-electroconduction mechanism to the point-electroconduction mechanism in a convex part of a polyhedron, the efficiency in electroconduction is improved. For the polyhedron, both a single kind and a combination of a plurality of kinds are acceptable.

The average particle size is preferably 0.1-1  $\mu\text{m}$ , more preferably 0.2-0.7  $\mu\text{m}$ . If the size is smaller than 0.1  $\mu\text{m}$ , the effect as a spacer might be lost. If the size is larger than 1  $\mu\text{m}$ , addition to its outermost layer might become impossible.

The resistance is preferably  $1\text{E}+7$  ( $1 \times 10^{<7>}$ )- $1\text{E}+10$  ( $1 \times 10^{<10>}$ )  $\Omega \cdot \text{cm}$ , more preferably  $1\text{E}+7$  ( $1 \times 10^{<7>}$ )- $1\text{E}+9$  ( $1 \times 10^{<9>}$ )  $\Omega \cdot \text{cm}$ . If the resistance is smaller than  $1\text{E}+7$   $\Omega \cdot \text{cm}$ , a charge property might be prevented. If the resistance is larger than  $1\text{E}+10$   $\Omega \cdot \text{cm}$ , adjustment of the resistance might become impossible, and the function as a magnetic powder might not be performed.

They are commercially available, for example, from Mitsui Metal Co. as Magnetite MG-1306 (octahedron) and Magnetite MG-3900 (polyhedron).

#### b. Silica

Silica, whose surface was hydrophobically treated and positively or negatively charged, can be used in the present invention.

The particle size is preferably equal to or smaller than 40 nm in primary size, more preferably 10-30 nm. If the size is larger than 40 nm, gaps between silica particles may become large and ruggedness is generated on the surface of the carrier.

As positively charged silica, for example, RA200HS (manufactured by Nippon Aerosol Co., Ltd.), 2015EP, and 2050EP (both Wacker Chemicals Co., Ltd) are commercially available. As negatively charged silica, for example, R812, RY200 (both manufactured by Nippon Aerosol Co., Ltd.), 2000, and 2000/4 (both Wacker Chemicals Co., Ltd) are commercially available.

It is preferable to add negatively charged silica to a positively charged toner, and to add positively charged silica to a negatively charged toner.

#### c. Fine particle resin

The following negatively charged resins (A) and positively charged resins (B) can be used as the fine particle resin according to the present invention.

##### A. Negatively charged resins

Fluorine-based resin (such as fluorovinylidene resin, tetrafluoroethylene resin, trifluorochloroethylene resin, and tetrafluoroethylene/hexafluoroethylene copolymer resin), vinyl chloride-based resin, and celluloid.

##### B. Positively charged resins

Acryl resin, polyamide-based resin (such as nylon-6, nylon-66, and nylon-11), styrene-based resin (polystyrene, ABS, AS, and AAS), chlorovinylidene resin, polyester-based resin (such as polyethylene terephthalate, polyethylene naphthalate, polybutylene terephthalate, polyacrylate, polyoxybenzoyl, and polycarbonate), polyether-based resin (such as polyacetal and polyphenylene ether), and ethylene-based resin (such as EVE, EEA, EAA, EMAA, EAAM, and EMMA).

It is preferable to add a negatively charged resin to a positively charged toner, and to add a positively charged resin to a negatively charged toner.

It is acceptable to contain both above-mentioned silica and particle resin as well as to contain one of them. In addition, one kind or a plurality of kinds of silica can be used, and one kind or a plurality of kinds of particle resin(s) can be used.

#### d. Coat thickness

The coat thickness of its outermost layer is preferably 0.1-6  $\mu\text{m}$ . If it is thinner than 0.1  $\mu\text{m}$ , coating might become incomplete. If it is thicker than 6  $\mu\text{m}$ , its outermost layer might be exfoliated by a mechanical impact such as friction from the outside.

#### e. Formation and fixing method of outermost layer

Formation and fixing method of outermost layer used in the present invention can be performed, depending on particle size and geometry of the magnetic powder to use and physical properties, such as particle size, solubility to organic solvents, melting point, and hardness, of silica and/or a resin, by selecting a method from the following two methods or by combining them.

##### (i) Fixing by mechanical impact

Its outermost layer is formed with a high-molecular-weight polyethylene-coated carrier core material and a



mixture that was prepared by mixing and an appropriate amount of magnetic powder or magnetic powder and silica and/or fine particle resin using a crusher such as the Henschel mixer (manufactured by Mitsui Miike Chemical Eng. Machine Co. Ltd., FM10L). The amount of magnetic powder or the amount of the mixture of magnetic powder and both or either silica and particle resin to be added then, are determined by resistance value to change, absolute value of charge quantity, and stability of real printing image density and other factors.

Although, concretely, it is usual to add at a weight ratio of 0.1-50 phr (additives per coating resin) per the amount of coating polyethylene of high-molecular-weight polyethylene-coated carrier, an appropriate ratio is around 20-30 phr, considering durability, change in resistance accompanying the formation of its outermost layer, stability in production, and other factors. Treatment using the Henschel mixer is conducted with the treating amount being in a range of 1-5 kg at such a low speed that magnetic powder, silica, and a fine particle resin, which were added, do not scatter.

Although treating time depends on the amount of magnetic powder to add, the amount of both or either silica and particulate resin to add, the amount of coating high-molecular-weight polyethylene to add, and other factors, it is necessary to conduct for 0.5-5 hrs. As dusts such as various kinds of particles are generated during fixation of magnetic powder and both or either silica and fine particle resin by this mechanical impact, classification may be carried out adequately.

## (ii) Thermal fixation by heating

Its outermost layer is formed by mixing the high-molecular-weight polyethylene resin-coated carrier and an appropriate amount of magnetic powder or a mixture prepared by mixing the magnetic powder and both or either silica and fine particle resin using a machine, which can heat, such as the Thermal Spheronizing Machine (Hosokawa Micron Co., Ltd.). The amount of magnetic powder and the amount of silica and/or fine particle resin to add then are determined by absolute value of charge quantity to change and stability of real printing image density.

Although, concretely, it is usual to add at a weight ratio of 0.1-50 phr (external additives per coating resin) per the amount of coating polyethylene of high-molecular-weight polyethylene-coated carrier, an appropriate ratio is 20-30 phr, considering durability and change in resistance accompanying the formation of its outermost layer, production stability.

In the thermal spheronization treatment, it is necessary to uniformly attach magnetic powder and both or either silica and a fine particle resin to the surface of the high-molecular-weight polyethylene resin-coated carrier before the treatment. For this purpose, a mixing treatment such as the ball-mill treatment, the V-blender treatment, and the Henschel-mixer treatment (for ca. 1 min) is carried out to electrostatically or mechanically attach the particles of magnetic powder and both or either silica and fine particle resin onto the surface of the high-molecular-weight polyethylene resin-coated carrier. Fixing was performed and an outermost layer is formed by heating for a very short time with uniformly attaching onto the surface of the high-molecular-weight polyethylene resin-coated carrier.

## 3. Electroconductive property of carrier

Although the optimal electroconductivity of a carrier depends on the system of the developer in which the carrier is used, a carrier showing a value of  $1 \times 10^{12}$  -  $1 \times 10^{14}$   $\Omega \cdot \text{cm}$  is preferred in general.

If the value is lower than  $1 \times 10^{12}$   $\Omega \cdot \text{cm}$ , carrier development and overlapping may occur. If the value is higher than  $1 \times 10^{14}$   $\Omega \cdot \text{cm}$ , deterioration in the quality of image such as lowering of the image density may occur.

Resistance values were determined by placing a carrier layer having an electrode area of  $5 \text{ cm}^2$ , a load of 1 kg, and a thickness of 0.5 cm, applying a voltage of 1-500 V to both upper and lower electrodes, measuring current values flowing in the bottom, and converting the values.

## II. Developer for electrophotography

The developer for electrophotography according to the

The developer for electrophotography according to the present invention can be obtained by mixing various toners with the above-mentioned carrier.

## 1. Toner

As a toner used in the present invention, the toner, which was produced according to a well-known method such as the suspension polymerization method, the crushing method, the microcapsule method, the spray dry method, and the mechanochemical method, can be used, and at least binder resins, coloring agents, and other additives such as electric charge-controlling agents, lubricants, off-set-preventing agents, and fixation-enhancing agents can be formulated, if necessary, to effectively improve a developing property and prevent scattering of a toner in the machine. In addition, fluidizing agents can also be added to improve its fluidizability. Binder resins which can be used are polystyrene-based resins such as polystyrene, styrene/butadiene copolymer, and styrene/acryl copolymer; ethylene-based copolymers such as polyethylene, ethylene/vinyl acetate copolymer, and ethylene/vinyl alcohol copolymer; epoxy-based resins; phenol-based resins; acryl phthalate resin; polyamide resin; polyester-based resins; and maleic acid resin. Coloring agents which can be used are well known dyes/pigments such as carbon black, Copper Phthalocyanine Blue, Indus Melia Blue, Peacock Blue, Permanent Red, Red Oxide, Alizarin Rake, Chrome Green, Malachite Green Rake, Methyl Violet Rake, Hansa Yellow, charge-controlling agents which can be used are positive electric charge-controlling agents such as nigrosin, nigrosin base, triphenylmethane-based compounds, polyvinylpyridine, and quaternary ammonium salt; and negative electric charge-controlling agents such as metal-complexes of alkyl-substituted salicylic acid (e.g. a chromium complex or a zinc complex of di-tert-butylsalicylic acid). Lubricants which can be used are Teflon, zinc stearate, and polyfluorovinylidene. Off-set-preventing/fixation-enhancing agents which can be used are a polyolefin wax or the like such as low-molecular-weight polypropylene and its modification. Magnetic materials which can be used are magnetite, ferrite, iron, and nickel. Fluidizing agents which can be used are silica, titanium oxide, aluminum oxide, or the like.

The average size of the toner is preferably equal to or lower than 20  $\mu\text{m}$ , more preferably 5-15  $\mu\text{m}$ .

## 2. Mixing ratio

The weight ratio of toner/carrier according to the present invention is 2-40wt.%, preferably 3-30wt.%, more preferably 4-25wt.%. If the ratio is lower than 2wt.%, the toner charge quantity becomes high, and enough image density is not given. If the ratio is higher than 40wt.%, enough charge quantity is not obtained, and the toner scatters from the developing machine and pollutes inside the copying machine, or causes toner-overlapping.

## 3. Usage

The developer according to the present invention is used in the 2- and 1.5-component-type electrophotography system such as the copying machine (analogue, digital, monochrome, and color type), the printer (monochrome and color type), and the facsimile, especially most suitably in the high-speed/ultra-high-speed copying machine and printer or the like in which the stress applied to the developer is high in the developing machine. There is no particular limitation to the type of image-formation, the type of exposure, the type (apparatus) of development, and various types of control (e.g. the type of controlling the density of a toner in a developing machine). One can adjust it to an optimal resistance, a particle size/particle size distribution, a magnetic power, and an charge quantity of the carrier and the toner, depending on the system.

## Examples

The examples of the present invention will be described more concretely below.

### Production of carrier

#### (1) Preparation of titanium-containing catalytic component

Into a 500-ml flask whose atmosphere was replaced for argon, 200 ml of dried n-heptane and 15 g (25

mmol) of magnesium stearate that had been dried at 120 DEG C under to make a slurry. After 0.44 g (2.3 mmol) of titanium tetrachloride was dropwise added with stirring, the content began to be heated, the reaction was carried out under reflux for 1 hour, and a clear viscous solution of a titanium-containing catalyst (the active catalyst) was obtained:

## (2) Evaluation of activity of titanium-containing catalytic component

Into a 1-liter autoclave whose atmosphere was replaced for argon, 400 ml of dried hexane, 0.8 mmol of triethylaluminum, 0.8 mmol of diethylaluminum chloride, and 0.004 mmol (as titanium atom) of the titanium-containing catalytic component obtained in (1) were added, and the content was heated up to 90 DEG C, wherein the inner pressure of the system was 1.5 kg/cm<sup>2</sup>G. After hydrogen was supplied up to 5.5 kg/cm<sup>2</sup>G, ethylene was continuously supplied maintaining the total pressure at 9.5 kg/cm<sup>2</sup>G. Polymerization was carried out for 1 hour, giving 70 g of polymer. The polymerization activity was 365 kg/g Ti/Hr, and MFR (melt flow rate at 190 DEG C, a loading of 2.16 kg according to JIS K 7210) of the polymer obtained was 40.

## (3) Production of polyethylene-coated carrier

Into a 2-liter autoclave whose atmosphere was replaced for argon, 960 g of sintered ferrite powder F-300 (Powder Tech Corp., average particle size 50  $\mu$ m) was added, the content was heated up to 80 DEG C, and drying was carried out under a reduced pressure (10 mmHg) for 1 hour. After the content was cooled down to 40 DEG C, 800 ml of dried hexane was added, and mixing was started. After 5.0 mmol of diethylaluminum chloride and the titanium-containing catalytic component described in (1) (0.05 mmol as titanium atom) were added, reaction was carried out for 30 min. Then the content was heated up to 90 DEG C, 4 g of ethylene was introduced, with the inner pressure being 3.0 kg/cm<sup>2</sup>G. After hydrogen was supplied up to 3.2 kg/cm<sup>2</sup>G, 5.0 mmol of triethylaluminum was added to start polymerization. The inner pressure of the system went down to and was stabilized at 2.3 kg/cm<sup>2</sup>G in ca. 5 min. Then a slurry containing 5.5 g of carbon black (Mitsubishi Chem. Co., MA-100) in 100 ml of dried hexane was added, polymerization was carried out continuously supplying ethylene, with keeping the inner pressure at 4.3 kg/cm<sup>2</sup>G for 45 min (the supply was stopped when 40 g of ethylene was introduced into the system), and 1005.5 g of carbon black-containing polyethylene resin-coated ferrite was obtained. Dried powder of it was uniformly black. Electron-microscopic observation revealed that the surface of the ferrite was coated with a thin polyethylene layer and the carbon black is uniformly dispersed in the polyethylene layer. Thermal gravimetric analysis (TGA) of the composite revealed that the weight ratio of ferrite/carbon black/polyethylene was 95.5/0.5/4.0.

The intermediate-step carrier obtained through this step was designated as "the carrier A1". The weight-average molecular weight of the coating polyethylene was 206,000.

Then carrier A1 was classified using a sieve of 125  $\mu$ m to remove particles which are equal to or larger than 125  $\mu$ m in diameter. The carrier after the classification was added into a fluidized-bed type gas-flow classifier having a height of 14 cm, and heated air (115 DEG C) was blown in to give at a linear velocity of 20 cm to fluidize the carrier for 10 hours. Thus carrier A2 was obtained.

### Example 1

Into a 10-liter Henschel mixer (Mitsui Miike Co., FM10L), 1000 g of the carrier A2 was added and mixed for 1 hr to give mechanical impact and to smoothen the surface of carrier A2. Then 8 g of magnetic powder (Mitsui Metal Co., Magnetite MG1306, octahedron) was added and mixed for another 1 hr to give mechanical impact to form outermost layer containing magnetic powder. To remove magnetic powder existing unfixed freely, the large particle size carrier and the aggregated magnetic powder were removed using a sieve. In addition, to remove particles such as the unfixed magnetic powder, treatment was carried out using a fluidized-bed type gas-flow classifier at a linear velocity of 20 cm for 2 hours. Thus carrier B was obtained.

### Example 2

Carrier C was obtained according to the same method as Example 1 except that 20 g of magnetic powder was used instead of 8 g. instead of 8 g.

### Example 3

Into a 10-liter Henschel mixer (Mitsui Miike Chemical Eng. Machine Co., Ltd. FM10L), 1000 g of the carrier A2 and mixed for 1 hr to give mechanical impact and to smoothen the surface of carrier A2. Then 8 g of magnetic powder (manufactured by Mitsui Metal Co., Ltd. Magnetite MG1306, octahedron) was added and mixed for another 1 hr to give mechanical impact, and 12 g of silica (manufactured by Nippon Aerosil Co., Ltd. R812) was added and mixed for another 1 hr to give mechanical impact, forming magnetic powder-silica-containing outermost layer. To remove magnetic powder existing unfixed freely, the large particle size carrier and the aggregated magnetic powder were removed using a sieve. In addition, to remove particles such as the unfixed magnetic powder, treatment was carried out using a fluidized-bed type gas-flow classifier at a linear velocity of 20 cm for 2 hours. Thus carrier D was obtained.

### Example 4

1000 g of the carrier A2 was placed into a 10-liter Henschel mixer (Mitsui Miike Chemical Machine Co., Ltd. FM10L). Then 8 g of the magnetic powder (manufactured by Mitsui Metal Co., Ltd. Magnetite MG1306, octahedron) and 8 g of a micropowdered resin (manufactured by Soken Kagaku Co., Ltd. MP2701) were added and mixed for 1 minute, whereby these were caused to adhere to the surface of the carrier A2 electrically and mechanically. Then, the mixture was heat-treated with heating air at 200 DEG C by using a thermal sphere forming machine (manufactured by Hosokawa Micron Co., Ltd. Thermal Sphere Forming Machine) to fix the magnetic powder and the micropowdered resin into the melted coating polyethylene resin layer, whereby the outermost layer mixed with the magnetic powder and the micropowdered resin was formed. The carrier with a large diameter, coagulated magnetic powder and coagulated micropowdered resin were removed by using sieve classification for the purpose of eliminating excesses of the magnetic powder and micropowdered resins existing free without being fixed. Also, the resultant product was processed using a fluidized-bed type air flow classification at an air flow linear velocity of 20cm for two hours for the purpose of eliminating excesses of the magnetic powder and micropowdered resins without being fixed. Thus carrier E was obtained.

### Example 5

Carrier F was obtained according to the same method as Example 1 except that Magnetite MG9300 (manufactured by Mitsui Metal Co., Ltd.) was used instead of Magnetite MG1306 (manufactured by Mitsui Metal Co., Ltd.).

### Comparative Example 1

Carrier A2 obtained in the carrier production example was not further treated.

### Comparative Example 2

According to the same method as Example 1 except that magnetic powder DFC450 (manufactured by Dowa Iron Powder Co., 25  $\mu$  m) was used instead of magnetic powder Magnetite MG1306 (Manufactured by Mitsui Metal Co., octahedron), a carrier was obtained, which could not be fixed because the particle size was too big.

### Comparative Example 3

Carrier G was obtained according to the same method as Example 1 except that Magnetite MG8200 (manufactured by Mitsui Metal Co., sphere) was used instead of Magnetite MG1306 (manufactured by Mitsui Metal Co.).

### Applied Example 1

Evaluation of real printing was carried out, using the toners A and B with respect to each of the carriers A2-G obtained in Examples 1-5 and Comparative Examples 1 and 3, using a machine that was modified from Ecosys 5 3550 (Kyocera Co.) in such a way that amorphous silicon was used as a photoreceptor when a positively charged toner was evaluated, that an organic electrophotography photoreceptor was used when a negatively charged toner was evaluated, and that the surface potential of the photoreceptor and the magnet roller bias potential could be adjusted. Results of evaluation of real printing, charge quantity, and static resistance are summarized in Table 1.

The followings were used as Toner A and Toner B:

Toner A: Styrene/n-butylmethacrylate copolymer resin 100 wt. parts

Carbon black (Mitsubishi Chem. Co., MA#8) 5 wt. parts

Dye (Orient Chem. Ind. Co., N07) 5 wt. parts

Toner A was obtained by adequately mixing the above materials using a ball mill, blending using three rolls heated at 140 DEG C, cooling the mixture by standing, and roughly crushing using a feather mill, and further finely crushing using a jet mill.

Toner B: Bisphenol A-based polyester resin 100 wt. parts

Carbon black (Cabot Corp., BPL) 8 wt. parts

Dye (Orient Chem. Ind. Co., E-84) 5 wt. parts

Toner B was obtained by adequately mixing the above materials using a ball mill, blending using three rolls heated at 140 DEG C, cooling the mixture by standing, and roughly crushing using a feather mill, and further finely crushing using a jet mill.

Evaluation of real printing was carried out by evaluating density of the printed part by using the Macbeth densitometer after printing at various bias potentials. Also static resistance and charge quantity were simultaneously measured. Measurement of charge quantity was carried out using a charge quantity-measuring device (Toshiba Chemical Co., Ltd. TB-200). The measurement was carried out by mixing 0.5 g of a toner and 9.5 g of a carrier, putting the mixture into a 500-ml plastic bottle, tumbling in a ball mill for 1 hr, at a blow pressure of 0.8 kg/cm<sup>2</sup>, for a blowing time of 50 sec, using a 500-mesh stainless steel sieve.

Id=Table 1 Columns=9 OR=L

Head Col 1: Kind of carrier

Head Col 2 to 3: Charge quantity (mu C/g)

Head Col 4: Static Resistance (OMEGA cm)

Head Col 5 to 9: Image density (Measured at each bias potential)

SubHead Col 1:

SubHead Col 2: Toner A

SubHead Col 3: Toner B

SubHead Col 4:

SubHead Col 5: 150V

SubHead Col 6: 200V

SubHead Col 7: 250V

SubHead Col 8: 300V

SubHead Col 9: 250V

Carrier A2 +11.2 -13.5 3.1E+11 1.17 1.23 1.30 1.32 1.33

Carrier B +10.9 -13.1 1.1E+10 1.19 1.27 1.35 1.44 1.53

Carrier C +11.0 -12.9 8.9E+08

Carrier D +18.2 -7.2 7.8E+12

Carrier E +7.5 -19.3 6.3E+13

Carrier F +11.2 -13.3 2.7E+11

Carrier G +10.8 -13.4 2.5E+10 1.21 1.24 1.29 1.32 1.34

Dependence of image density on magnet roller bias potential in Applied Example 1 is illustrated in Fig. 1.

As it is clear from the description above, by making the geometry of magnetic powder to add to an outermost layer of the carrier for electrophotography, which is used as a developer for electrophotography, octahedron or the like, the proportional relation between bias potential and image density is obtained, the increasing rate of image density is still high even at a high bias potential, and obtaining clear light and shade in printing and stable image becomes possible.

Applied Example 2

Carriers B, A2, or G obtained in Example 1, Comparative Example 1, or Comparative Example 3, respectively, was mixed with a toner (Kyocera Corporation, Ecotone(trademark)) at a toner concentration of 5 wt.% (T/C), loaded into a Printer FS3550 (Kyocera Corporation, Ecosys (trademark)), and evaluation of continuous printing was carried out. The result is summarized in Fig. 2.

#### Industrial Applicability

As described above, the present invention can provide a carrier for electrophotography, which is excellent in durability and a charging property, gives clearer light and shade in real printing than the conventional one, and allows fine and free adjustment of static resistance and charge quantity, and a developer using the carrier.

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